

GRASAS Y ACEITES, 60 (4),  
JULIO-SEPTIEMBRE, 360-366, 2009,  
ISSN: 0017-3495  
DOI: 10.3989/gya.010309

## Oxidation of ethoxylated fatty alcohols to alkylpolyglycol carboxylic acids using noble metals as catalysts

By Spiros Zlatanov,<sup>a,\*</sup> Kostas Laskaridis<sup>a</sup> and Angelos Sagredos<sup>a</sup>

<sup>a</sup> Chemical Engineering Department, Aristotle University of Thessaloniki,  
54124 Thessaloniki, Greece.

(\*corresponding author: szlatano@eng.auth.gr)

### RESUMEN

**Oxidación de alcoholes grasos etoxilados a ácidos carboxílicos alquilpoliglicólicos usando metales nobles como catalizadores.**

La conversión de alcoholes grasos etoxilados a los correspondientes ácidos carboxílicos por deshidrogenación/oxidación con metales nobles como catalizador ha sido estudiada. Alcoholes primarios alifáticos etoxilados, alcoholes alifáticos secundarios etoxilados al azar y alquilfenoles etoxilados han sido convertidos a los correspondientes ácidos en presencia de base. Los catalizadores paladio y platino fueron usados sin degradación significativa de las cadenas etoxiladas con un rendimiento que excedió del 90%. Por otra parte catalizadores de rodio y rutenio produjeron rendimientos del 80 y 60%, respectivamente.

**PALABRAS CLAVE:** Ácido carboxílico alquilpoliglicólico – Ácido carboxílico etoxilado – Alcohol graso etoxilado – Deshidrogenación catalizada por metales nobles – Oxidación catalizada por metales nobles.

### SUMMARY

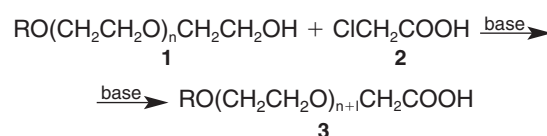
**Oxidation of ethoxylated fatty alcohols to alkylpolyglycol carboxylic acids using noble metals as catalysts**

The conversion of ethoxylated fatty alcohols to the corresponding carboxylic acids through dehydrogenation/oxidation using noble-metal catalysts has been studied. Ethoxylated primary aliphatic alcohols, ethoxylated random secondary aliphatic alcohols and ethoxylated alkylphenols have been converted to the corresponding acids in the presence of a base. The noble metal catalysts Palladium and Platinum were used without significant degradation of the ethoxyl chain in yields that exceeded 90%. On the other hand, the catalysts Rhodium and Ruthenium gave yields of about 80% and 60% respectively.

**KEY-WORDS:** Alkylpolyglycol carboxylic acid – Ethoxy carboxylic acid – Fatty alcohol ethoxylate – Noble-metal catalyst Oxidation – Noble-metal catalyst Dehydrogenation.

### 1. INTRODUCTION

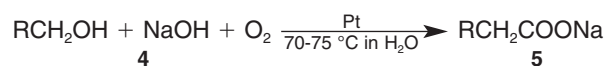
Alkylpolyglycol carboxylic acids (3) were already prepared by the reaction of ethoxylated alcohols (1) with chloracetic acid (2) (Aalbers, 1964):



This method gives maximum conversion up to 90%, but the process is less practical because chloracetic acid is a strong acid and an environmental contaminant with etching, corrosive and toxic properties. The extensive application of this method demands diligent safety measures for the workers and the environment and makes it inconvenient and expensive. In addition, the product of this reaction is not the corresponding carboxylic acid with the same carbon chain as the ethoxylated alcohol, but an acid with two additional carbons.

Oxidation with conventional oxidants (among others  $\text{KMnO}_4$ ) and autoxidation in the presence of soluble transition-metal catalysts give poor yields according to our experience.

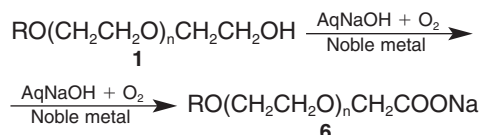
The oxidation of primary alcohols to acids with oxygen using platinum catalyst has been reported previously in the literature (Heyns *et al.*, 1957, Heyns *et al.*, 1960, Heyns *et al.*, 1962, Bekkum, 1990, Roper, 1990, Vinke *et al.*, 1992, Haines *et al.*, 1998). Alcohols could be converted to salts of the corresponding acids in the presence of bases ( $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ) in yields which depend on the structure of the alcohol.



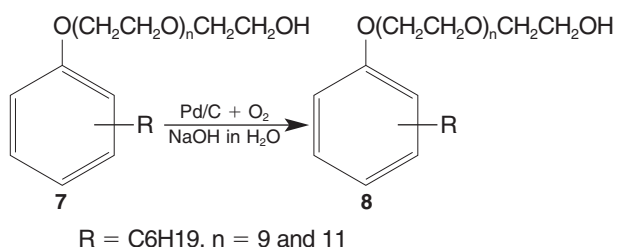
Further studies conducted by Mallat and Baiker (Mallat *et al.*, 1994, Mallat *et al.*, 1995) regarding the oxidation of alcohols with molecular oxygen to the respective acids using platinum catalysts have shown that the participation of a second metal (mainly Bi and Pb) is useful as a reaction promoter. Furthermore, the effect of the pH on the oxidation rate has been comprehensively studied as well as its effect on the route of the reaction (Mallat *et al.*, 1994, Gangwal *et al.*, 2004). Finally, recent studies

(Korovchenko *et al.*, 2007, Sheldon *et al.*, 2000, Zhan *et al.*, 2004, Mallat *et al.*, 1995) are concentrated on the conditions that increase the yield of the produced acids, or aldehydes, after oxidising primary alcohols with a platinum catalyst. In this way oxygen becomes the most useful reagent as it is not toxic and its supply is readily available and inexpensive.

The aim of this work was a convenient oxidation of ethoxylated primary and secondary aliphatic alcohols (1, R = alkyl)



as well as of ethoxylated alkylphenols (7, R = alkyl)



to the corresponding alkylpolyglycol carboxylic acids using platinum and other noble catalysts with oxygen in an aqueous alkaline solution (6 and 8).

This noble-metal catalysed oxidation was considered to be of great interest for the synthesis of alkylpolyglycol carboxylic acids as it gives high yields without degradation or elongation of the ethoxyl chain and avoids environmental problems. In addition, this reaction is achieved with relatively low costs because of the small amount of catalysts it requires and the possibility of regenerating them.

## 2. MATERIALS AND METHODS

### 2.1. Catalysts and Reagents

In the present study the noble metals Platinum (as PtO<sub>2</sub>, reduced in situ for 6 hr with hydrogen to Pt, Merck), Palladium (10% on charcoal, Merck), Rhodium (5% on charcoal, Merck), Ruthenium (10% on charcoal, Merck) were used as catalysts according to Schiller (1955).

Three types of fatty alcohols were employed, selected as representing different ethoxy-(EO) chain lengths and two different modes of attachment of ethoxy chain to hydrophobe chain.

#### Ethoxylated *n*-primary alcohols

A mixture was made of approximately 60% 1-dodecanol (compound **1**, with R = C<sub>12</sub>H<sub>25</sub> and n = 2) and 40% 1-tetradecanol (**1**, with R = C<sub>14</sub>H<sub>29</sub> and

n = 2) ethoxylated with 3 EO units (Union Carbide). The following analytical data were determined for the IR-spectrum: Strong broad OH absorption at 3470 cm<sup>-1</sup>, strong broad C–H absorption at 2960 – 2840 cm<sup>-1</sup>, strong broad C–O–C absorption at 1160 – 1050 cm<sup>-1</sup>, No COOH absorption at 1750 cm<sup>-1</sup>. Hydroxyl-Value 174 (according to DIN 53240). Molecular weight was 321 (calculated from the Hydroxyl-Value).

A mixture was made of approximately 60% 1-dodecanol (compound **1**, with R = C<sub>12</sub>H<sub>25</sub> and n = 4) and approximately 40% 1-tetradecanol (**1**, with R = C<sub>14</sub>H<sub>29</sub> and n = 4) ethoxylated with 5 EO (Union Carbide). The following analytical data were determined for the IR-spectrum: Strong broad OH absorption at 3470 cm<sup>-1</sup>, strong broad C–H absorption at 2960 – 2840 cm<sup>-1</sup>, strong broad C–O–C absorption at 1160 – 1050 cm<sup>-1</sup>, No COOH absorption at 1750 cm<sup>-1</sup>. Hydroxyl-Value 140 (according to DIN 53240). Molecular weight was 400 (calculated from the Hydroxyl-Value).

#### Ethoxylated *sec*-alcohols

A mixture of random hydroxylated secondary tetradecanols (compound **1**, with R = iso-C<sub>14</sub>H<sub>29</sub> and n = 2) and *sec* pentadecanols (compound **1**, with R = iso-C<sub>15</sub>H<sub>31</sub> and n = 2) ethoxylated with 3 EO, where the ethoxyl group attached randomly to all secondary hydroxyl groups (Union Carbide) was used. The following analytical data were determined for the IR-spectrum: Strong broad OH absorption at 3470 cm<sup>-1</sup>, strong broad C–H absorption at 2960 – 2840 cm<sup>-1</sup>, strong broad C–O–C absorption at 1160 – 1050 cm<sup>-1</sup>, no COOH absorption at 1750 cm<sup>-1</sup>. Hydroxyl-Value 159 (according to DIN 53240). Molecular weight was 352 (calculated from the Hydroxyl-Value).

#### Ethoxylated alkylphenols

Nonylphenol ethoxylated with 10 EO (compound **7**, with R = C<sub>9</sub>H<sub>19</sub> and n = 9) (Degussa-Hüls) was applied. The following analytical data were determined for the IR-spectrum: Strong broad OH absorption at 3470 cm<sup>-1</sup>, strong broad C–H absorption at 2960 – 2840 cm<sup>-1</sup>, strong broad C–O–C absorption at 1160 – 1050 cm<sup>-1</sup>, no COOH absorption at 1750 cm<sup>-1</sup>. Hydroxyl-Value 85 (according to DIN 53240). Molecular weight 659 (calculated from the Hydroxyl-Value).

Nonylphenol ethoxylated was mixed with 12 EO (compound **7**, with R = C<sub>9</sub>H<sub>19</sub> and n = 11) (Degussa-Hüls). The following analytical data were determined for the IR-spectrum: Strong broad OH absorption at 3470 cm<sup>-1</sup>, strong broad C–H absorption at 2960 – 2840 cm<sup>-1</sup>, strong broad C–O–C absorption at 1160 – 1050 cm<sup>-1</sup>, no COOH absorption at 1750 cm<sup>-1</sup>. Hydroxyl-Value 78 (according to DIN 53240). Molecular weight 718 (calculated from the Hydroxyl-Value).

## 2.2. Oxidation of ethoxylated n-primary alcohols with Platinum

### *Oxidation of ethoxylated n-primary alcohol with 3 EO units*

A 500-ml round bottom flask fitted with thermometer, gas inlet tube, mechanical stirrer, reflux condenser and heating jacket with temperature control was employed. The charge consisted of 1,16 g Platindioxid ( $\text{PtO}_2$ ), 20 g ethoxylated n-primary alcohol with 3 EO units (as described under 2.1), 4,8 g  $\text{NaHCO}_3$  (Merck) and 210 ml water.

The procedure described in brief entails 170ml of water and 1.16g  $\text{PtO}_2$  put in the reaction flask where nitrogen was bubbled through the stirred suspension to expel any oxygen. Hydrogen in a ratio of 80 ml/min was then passed through the suspension for 30 min at room temperature to activate the catalyst. After interruption of the hydrogen flow, nitrogen was flushed again to remove any residual amount of hydrogen or oxygen, as this could be explosive. 4,8 g of sodium hydrogen carbonate dissolved in 40 ml of water were then added and the suspension was heated up to 80 °C. At this temperature, 20 g ethoxylated n-primary alcohol with 3 EO units was added. Oxygen was then supplied to the mixture at a rate of 135 ml/min. The reaction mixture was vigorously stirred for 2 h at 68-70 °C, while the oxygen uptake was measured with a gas burette. After completion of the reaction, the mixture was filtered, the filtrate was acidified to pH-1 with concentrated hydrochloric acid and the solvent was extracted with chloroform. The combined extracts were washed with a saturated (at 20 °C) sodium sulfate solution until the absence of chloride ( $\text{AgNO}_3$  test), dried with anhydrous sodium sulfate and the solvent was evaporated to dryness under vacuum. The product was obtained as a colorless liquid.

### *Oxidation of ethoxylated n- primary alcohol with 5 EO units*

The oxidation was carried out in the experimental configuration described under "Oxidation of ethoxylated n-primary alcohol with 3 EO units" section. The charge consisted of 10g Palladium, 10% on charcoal (1g Pd), 30 g ethoxylated n- primary alcohol with 5 EO units, 210 ml water and 2.3 g NaOH (Merck).

The procedure described in brief entails 160ml of water and 10g Pd-catalyst put in the reaction flask where hydrogen was bubbled through the stirred suspension with a flow rate of 80 ml/min for 25 min at room temperature. Sodium hydroxide dissolved in 50 ml of water was added, then the hydrogen flow was released for an additional 5 min and the suspension was heated up to 80 °C. At this temperature, 30g ethoxylated n-primary alcohol with 5 EO was added. Nitrogen was used for the removal of hydrogen. Finally, oxygen was carried

through the vigorously stirred reaction mixture at a flow rate of 135 ml/min. The temperature was between 79–84 °C, the reaction time 150 min, while oxygen uptake was measured with a gas burette. The catalyst was filtered off; the filtrate was acidified with concentrated HCl and extracted with chloroform. The extraction procedure was repeated twice. At the end, the extract was washed with sodium sulfate (10% aqueous solution) to remove any inorganic acid and filtered. The acid was obtained as a colourless liquid after evaporation of the solvent under vacuum.

## 2.3. Oxidation of ethoxylated sec alcohols with Palladium

The oxidation was carried out in the experimental configuration described under the "Oxidation of ethoxylated n-primary alcohol with 3 EO units" section. The charge consisted of 10 g Palladium, 10% on charcoal (1g Pd), 22 g randomly hydroxylated sec. tetradecanols and pentadecanols ethoxylated with 3 EO units, 3.5 g KOH (Merck) and 420 ml water. The oxidation and the isolation of the product were carried out as described under the "Oxidation of ethoxylated n- primary alcohol with 5 EO units" section. However, the catalyst was suspended in 340ml water and the nonionic diluted in 80ml water. The reaction temperature was between 85 – 89 °C and the reaction time was 90 min. The obtained product was a pale yellow liquid.

## 2.4. Oxidation of ethoxylated nonylphenol with Palladium

### *Oxidation of ethoxylated nonylphenol with 10 EO units*

The oxidation was carried out in the experimental configuration described under the "Oxidation of ethoxylated n-primary alcohol with 3 EO units" section. The charge consisted of 10g Palladium, 10% on charcoal (1g Pd), 30 g ethoxylated nonylphenol with 10 EO units, 210 ml water and 2.3 g NaOH (Merck). The oxidation and the isolation of the product were carried out as described under the "Oxidation of ethoxylated n-primary alcohol with 5 EO units" section. However, the reaction temperature was between 80-83 °C and the reaction time 90 min. The obtained product was a pale yellow liquid.

### *Oxidation of ethoxylated nonylphenol with 12 EO units*

The oxidation was carried out in the experimental configuration described under the "Oxidation of ethoxylated n-primary alcohol with 3 EO units" section. The charge consisted of 10 g Palladium, 10% on charcoal (1g Pd), 30 g ethoxylated nonylphenol with 12 EO units, 120 ml water and 2.2 g NaOH ((Merck). The oxidation and

the isolation of the product were carried out as described under the "Oxidation of ethoxylated n-primary alcohol with 5 EO units" section. However, the reaction temperature was between 80-83 °C. The obtained product was a pale yellow liquid.

## 2.5. Yield determination of the ethoxy carboxylic acids using an ion-exchange column

A Dowex 21K column was used to perform the ion-exchange analysis. The resin contained in the column exceeded four times the theoretical amount (calculated from the Acid Value). The resin was initially washed with NaOH (2N) until all chloride was removed (AgNO<sub>3</sub> test), then with water until the pH turned to neutral and finally with methanol until all water was removed.

A sample containing 3-5 g of each reaction product (obtained from the ethoxylated alcohols) was applied to the column and then eluted with methanol. By applying methanol the neutral material of the sample was eluted from the column and obtained at a later time with evaporation.

A second elution was performed with a mixture containing CH<sub>3</sub>OH and concentrated HCl (9:1 v/v) until the whole column length changed its colour to light yellow. This second eluate was left for a minimum of 2 hours at room temperature to complete the esterification of the eluted acids. The majority of the methanol contained in the second eluate was then separated from the mixture by applying evaporation under vacuum at 20 °C. The

concentrate was taken up in water and the resultant solution was extracted with chloroform. The chloroform-phase was washed with aqueous sodium sulfate until the absence of any residual chloride, and dried over sodium sulfate. After evaporation of the solvent, the methyl ester of the ethoxy carboxylic acids were obtained and weighed. From their weight the initial amount of free acids was calculated.

## 2.6. Further experiments with Platinum, Palladium, Rhodium and Ruthenium

Further experiments on the oxidization of ethoxylated alcohols to corresponding acids with Platinum catalyst were carried out as described under the "Oxidation of ethoxylated n-primary alcohol with 3 EO units" section and with Palladium, Rhodium and Ruthenium catalysts as described under the "Oxidation of ethoxylated n- primary alcohol with 5 EO units" section. The reaction conditions are presented in table 1.

## 3. RESULTS

### 3.1. Analytical data of the reaction products

The reaction products described in sections 2.2-2.4 are presented in table 2. According to these the yields, the reaction products varied between 19.6 and 28.6%. All of the products showed a strong absorption at 1750 and 1120 cm<sup>-1</sup> which is

Table 1  
Oxidation of ethoxylated n-primary alcohols and secondary alcohols with noble catalysts

Experiment Number	Noble Metal Catalyst	Charge Ratios			Base (mole/ mole non-ionic)	Temperature (°C)	Time (min)	Nonionic
		Catalyst	Nonionic	Water				
1	Pt	1	30	210	NaOH	79-83	150	n-alc.3EO <sup>1</sup>
2	Pt	1	30	210	NaOH	79-83	150	n-alc.3EO
3	Pt	1	20	210	NaHCO <sub>3</sub>	68-70	120	n-alc.3EO
4	Pd	1	20	300	NaHCO <sub>3</sub>	78-82	120	n-alc.3EO
5	Pd	1	30	210	NaHCO <sub>3</sub>	78-82	120	n-alc.3EO
6	Pd	1	30	210	NaOH	79-84	150	n-alc.3EO
7	Pd	1	20	300	NaHCO <sub>3</sub>	75-78	120	n-alc.3EO
8	Pd	1	20	140	NaHCO <sub>3</sub>	72-77	300	n-alc.3EO
9	Ru	1	20	210	NaOH	84-91	210	n-alc.3EO
10	Ru	1	15	210	NaOH	84-93	180	n-alc.3EO
11	Rh	1	30	300	NaOH	84-91	150	n-alc.3EO
12	Rh	1	30	210	NaOH	85-90	90	n-alc.3EO
13	Pd	1	28	210	NaOH	80-85	150	n-alc.5EO <sup>2</sup>
14	Pd	1	30	210	NaOH	80-85	150	n-alc.5EO
15	Pd	1	15	210	NaOH	85-90	135	n-alc.5EO
16	Pd	1	30	210	NaOH	78-82	80	sec-alc.3EO <sup>3</sup>
17	Pd	1	22	420	KOH	85-89	150	sec-alc.3EO
18	Pd	1	30	210	NaOH	80-83	150	Alkylphenol 10EO <sup>4</sup>
19	Pd	1	30	120	NaOH	80-82	150	Alkylphenol 12EO <sup>5</sup>

1) n-alc.3EO = mixture of approximately 60% 1-dodecanol and approximately 40% 1-tetradecanol ethoxylated with 3 EO units.

2) n-alc.5EO = mixture of approximately 60% 1-dodecanol and approximately 40% 1-tetradecanol ethoxylated with 5 EO units.

3) sec-alc.3EO = mixture of random hydroxylated secondary tetradecanols and secondary pentadecanols ethoxylated with 3 EO units.

4) alkylphenol 10EO = ethoxylated Nonylphenol with 10 EO units.

5) alkylphenol 12EO = ethoxylated Nonylphenol with 12 EO units.



Table 2  
Analytical Data of the Reaction Products

	Catalyst	Yield	IR – spectrum absorption			Aromatic Band			Acid Value
			COOH	C–O–C	OH				
Alcohol			1750 cm <sup>-1</sup>	1120 cm <sup>-1</sup>	3500 cm <sup>-1</sup>	750 cm <sup>-1</sup>	1510 cm <sup>-1</sup>	1610 cm <sup>-1</sup>	
n- primary 3 E.O.	Pt	19,6 g	Strong	Strong	Absent	Absent	Absent	Absent	164,0
n- primary 5 E.O.	Pd	28,1 g	Strong	Strong	Absent	Absent	Absent	Absent	124,2
sec 3 E.O.	Pd	28,6 g	Strong	Strong	Absent	Absent	Absent	Absent	141,3
Nonylphenol 10 E.O.	Pd	27,0	Strong	Strong	Absent	Medium	Medium	Medium	74,2
Nonylphenol 12 E.O.	Pd	26,0	Strong	Strong	Absent	Medium	Medium	Medium	67,8

characteristic of the carboxyl group and the C–O–C bound respectively. On the other hand, no absorption was present at 3500 cm<sup>-1</sup> which indicates the absence of the hydroxyl group. From these data the conversion of the majority of the initial amount of alcohol could be concluded. Also both products prepared from nonylphenol showed characteristics of aromatic compound absorptions at 750, 1510 and 1610 cm<sup>-1</sup>.

### 3.2. Purities and yields of the reaction products

The acid value of the oxidation products was determined at the end of the reaction according to the DGF-method C-V 2 (81). The measured acid value compared with the theoretical value was used for the calculation of product purity. In addition, the yield of the products was determined with the ion exchange column. In this way, the degradation of

the ethoxy-chain can be calculated from the comparison of the purity (derived from the acid value) and the yield (derived from the ion-exchange column). The results are presented in Table 3.

## 4. DISCUSSION

The results show that all three types of ethoxylated alcohols used in the current study (n-primary fatty alcohols, random hydroxylated sec alcohols and alkylphenols) can be oxidised with oxygen using noble metal catalysts. All the catalysts used in alkaline aqueous solutions are suitable for the oxidation of the ethoxylated alcohols to the corresponding acids with virtually no degradation of the ethoxyl chain.

The obtained products are colourless to pale-yellow liquids. The ethoxy carboxylic acids produced from the ethoxylated n-primary alcohol with 3 EO

Table3  
Purity of the reaction products calculated from the acid value and yields calculated from the ion exchange column

Experiment Number	Nonionic	Purity	Yield	Remarks
1	n-alc.3EO <sup>1</sup>	90	89	See 2.2.1
2	n-alc.3EO	92	90	
3	n-alc.3EO	99	–	
4	n-alc.3EO	93	92	
5	n-alc.3EO	93	–	
6	n-alc.3EO	96	–	Catalyst used for second time without any special treatment
7	n-alc.3EO	75	–	
8	n-alc.3EO	76	–	
9	n-alc.3EO	63	59	
10	n-alc.3EO	55	52	
11	n-alc.3EO	80	75	See 2.2.2
12	n-alc.3EO	74	67	
13	n-alc.5EO <sup>2</sup>	90	89	
14	n-alc.5EO	92	90	
15	n-alc.5EO	97	–	
16	sec-alc.3EO <sup>3</sup>	85	83	See 2.3
17	sec-alc.3EO	93	91	
18	Alkylphenol 10EO <sup>4</sup>	89,5	88	See 2.4.1
19	Alkylphenol 12EO <sup>5</sup>	89	87	See 2.4.2

1) n-alc.3EO = mixture of approximately 60% 1-dodecanol and approximately 40% 1-tetradecanol ethoxylated with 3 EO units.

2) n-alc.5EO = mixture of approximately 60% 1-dodecanol and approximately 40% 1-tetradecanol ethoxylated with 5 EO units.

3) sec-alc.3EO = mixture of random hydroxylated secondary tetradecanols and secondary pentadecanols ethoxylated with 3 EO units.

4) alkylphenol 10EO = ethoxylated Nonylphenol with 10 EO units.

5) alkylphenol 12EO = ethoxylated Nonylphenol with 12 EO units.

units and the randomly hydroxylated sec alcohols with 3 EO units are hardly soluble in water. The ethoxy carboxylic acids derived from the n-primary alcohol with 5 EO units as well as the ethoxylated alkylphenols with 10 or 12 EO units dissolve well in water.

The ethoxylated aliphatic alcohols and alkylphenols were converted to carboxylic acids in high yields (exceeding 90%) when Palladium and Platinum catalysts were used. The other two catalysts show poorer conversion amounts. In fact, yields of about 80% were achieved using Rhodium and of about 60% using Ruthenium.

According to the results, it can be concluded that the catalytic effect of Platinum was comparable to that of Palladium. Both catalysts are highly efficient for the catalysis of the dehydrogenation/oxidation process of the ethoxylated alcohols in the alkaline solution without significant degradation of the ethoxyl chain. Rhodium and Ruthenium gave significantly lower yields and a degradation of the ethoxyl group could be assumed.

The extension of a possible degradation was determined by applying an ion-exchange column. This method provides an independent test for the purity of the obtained products based on the gravimetric determination of the methylated ethoxy carboxylic acids. The comparison of the purities calculated from the acid value and the yields determined by the ion-exchange column give the amount of the degradation of the ethoxyl chain. From the results, a marginal degradation of about 1-2% by using Pt or Pd and a higher degradation of about 6-9% by using Rh or Ru catalysts were determined.

The temperature and the concentration of the ethoxylated alcohols in water are important factors for the conversion to ethoxy carboxylic acids. The reaction proceeds satisfactorily at 80-90 °C with concentrations of ethoxylated primary and sec alcohols in water under 14%. At higher concentrations the reaction begins with a fast oxygen uptake but the reaction mixture becomes rapidly semi-solid. This leads to a low conversion probably due to the poor contact of the substrate, the catalyst and oxygen. The reactions of the ethoxylated alkylphenols with 10 and 12 EO units also result in satisfactory conversions at higher concentrations of about 25% because of the better solubility of the product in the alkaline solution.

The presence of a base is also important. In aqueous alkaline solutions the Pd-catalysed oxidation of the n-primary alcohol with 3 EO units is almost complete in 2-4 hours. The same reaction without the use of a base proceeded significantly slower and gave a conversion smaller than 70% after 7 hours. At higher concentrations of nonionic in water, NaOH or KOH are more suitable than NaHCO<sub>3</sub>.

Another important reaction factor is the weight ratio of catalyst to nonionic. A ratio of catalyst consisting of non ionic of 1:15 in most cases results in higher conversion yields than a ratio of 1:30. However, in some cases (reactions 1, 2, 6, 7, 11 and 13 presented in Table 1) an increase in this ratio has

no effect on the conversion ratio. In every case, due to the high cost of the catalyst compared with the limited improvement of the conversion, an increase in the catalyst to non ionic ratio is not applicable.

The use of Palladium is encouraged for further investigations as this catalyst is less expensive than Platinum. Also, further investigations with multiple uses of Palladium are recommended since, as in initial trials in this work (experiments 7, 8 described in Table 1), the reuse of the catalyst had some success but further studies are required to define the life-time and losses in the catalyst.

## 5. CONCLUSIONS

Ethoxylated n-primary and secondary aliphatic alcohols, as well as ethoxylated alkylphenols, can be converted to the corresponding carboxylic acids in yields over 90% by oxidation with oxygen in the presence of a base (NaOH, KOH, NaHCO<sub>3</sub>) using palladium and platinum without significant degradation of the ethoxyl chain. Rhodium and ruthenium are less efficient as catalysts and gave, in comparison, lower yields of about 80% (Rh) and 60% (Ru) and some ethoxyl chain degradation.

## REFERENCES

- Aalbers JG. 1964. Lauryl (poly-1-oxapropene) oxaethane carboxylic acids, Drukkerij Wed. G. Van Soenst N. V., Amsterdam.
- Gangwal VR, van der Schaaf J, Kuster BFM, Schouten JC. 2005. Influence of pH on noble metal catalysed alcohol oxidation: reaction kinetics and modeling. *J. Catal.* **229**, 389-403.
- Haines AH. 1988. Methods for the Oxidation of Organic Compounds: Alcohols, Alcohol Derivatives, Alkyl Halides, Nitroalkanes, Alkyl Azides, Carbonyl Compounds, Hydroxyarenes, and Aminoarenes, *Academic Press, London*.
- Heyns K, Paulsen H. 1957. Neuere Methoden der präparativen organischen Chemie II. 8. Selektive katalytische Oxydationen mit Edelmetall-Katalysatoren. *Angew. Chem.* **69**, 600-608.
- Heyns K, Blazejewicz L. 1960. Katalytische oxydation von primären und sekundären hydroxylverbindungen mit sauerstoff am platinkontakt in flüssiger phase: Über katalytische oxydationen—XIV, *Tetrahedron* **9**, 67-75.
- Heyns K, Paulsen H. 1962. Selective catalytic oxidation of carbohydrates, employing platinum catalysts. *Adv. Carbohydr. Chem.* **17**, 169-221.
- Korovchenko P, Donze C, Gallezot P, Besson M. 2007. Oxidation of primary alcohols with air on carbon-supported platinum catalysts for the synthesis of aldehydes or acids, *Catal. Today* **121**, 13-21.
- Mallat T, Baiker A. 2004. Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chem. Rev.* **104**, 3037-3058.
- Mallat T, Baiker A. 1995. Catalyst potential: a key for controlling alcohol oxidation in multiphase reactors. *Catal. Today* **24**, 143-150.
- Mallat T, Baiker A. 1994. Oxidation of alcohols with molecular oxygen on platinum metal catalysts in aqueous solutions. *Catal. Today* **19**, 247-284.

- Röper H. 1990. in: F.W. Lichtenthaler (Ed.) Carbohydrates as Organic Raw Materials, VCH, *Weinheim*, pp. 267-288.
- Schiller G. 1990. in: Houben, Weyl, Müller (Eds.), Methoden der Organischen Chemie, 4th edition, *Georg Thieme Verlag*, Stuttgart, p.339.
- Sheldon RA, Arends IWCE, Dijkman A. 2000. New developments in catalytic alcohol oxidations for fine chemicals synthesis. *Catal. Today* **57**, 157-166.
- van Bekkum H. 1990. in: F.W. Lichtenthaler (Ed.) Carbohydrates as Organic Raw Materials, VCH, *Weinheim*, pp. 289-310.
- Vinke P, de Wit D, de Goede ATJW, van Bekkum H. 1992. in: Ruiz P., Delmon B. (Eds.) Studies in Surface Science and Catalysis, Vol. 72: New Developments in Selective Oxidation by Heterogeneous Catalysis, *Elsevier Amsterdam*, pp.1-20.
- Zhan BZ, Thompson A. 2004. Recent developments in the aerobic oxidation of alcohols. *Tetrahedron* **60**, 2917-2935.

Recibido: 7/1/09

Aceptado: 6/2/09